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**DAMAGE OF CONCRETE PARKING
APRONS FROM AUXILIARY POWER
UNIT (APU) EXHAUST AND SPILLED
JET OILS**

**MICHAEL C. McVAY, JIM MURFEE,
CHARLIE W. MANZIONE**

**HEADQUARTERS AIR FORCE CIVIL
ENGINEERING SUPPORT AGENCY
AIR BASE OPERABILITY AND REPAIR
BRANCH**

TYNDALL AFB, FL 32403-6001

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13. ABSTRACT (Maximum 200 words) The precise cause for concrete damage observed in the vicinity of parked B-1 and F/A-18 aircraft has been determined. The combination of downward-directed auxiliary power unit (APU) blast and spilled aircraft oils are responsible for the scaling observed at these sites. Laboratory tests confirmed that ester-based lubricating oils and hydraulic fluids are chemically reacting with the calcium hydroxide in the concrete and destroying the mortar-aggregate bonds. The cyclic heating of the pavement by the APU greatly accelerates the reaction and facilitates the mixing and refluxing of aircraft fluids with the aqueous calcium hydroxide present. A variety of sophisticated tests were conducted to verify these findings, including X-ray diffraction and mass spectroscopy. In addition, the damage observed at military installations was duplicated under controlled laboratory conditions. After five weeks of subjecting a test slab to cyclic heat and jet oils, damage similar to that observed in the field was produced.				
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13. (continued) No damage was observed to the test slab that underwent cyclic heating alone. Potential solutions to the APU-oils problems are offered; these need to be tested in the laboratory prior to field application.

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EXECUTIVE SUMMARY

A. OBJECTIVE

Determine the cause of concrete damage under auxiliary power units (APUs) and propose solutions.

B. BACKGROUND

Both the United States Air Force and Navy have reported concrete scaling on their respective B-1 and F/A-18 parking aprons. This damage is a source of possible foreign object damage (FOD) and is not tolerated by operators. Installation engineers report the damage to be in areas of APU jet blast impingement, where large amounts of spilled lubricants, hydraulic fluids and jet fuels have been noted. The fluids are either vented by the aircraft or spilled during maintenance.

Esters, which are chemically-combined acids and alcohols, will break down (hydrolyze) when heated in an aqueous acid or base solution. Discussions with Hatco, a major manufacturer of raw materials in lube oils and hydraulic fluids, reveal that 90 to 95 percent of lubricating oils are composed of ester blends. Hydraulic fluid is 60 to 70 percent hydrocarbons and 30 to 35 percent esters.

If the oils and/or hydraulic fluids were undergoing hydrolysis, it would have to be of an alkaline variety, since the pH of concrete may be as high as 11 or 12. This is due to the strong base, calcium hydroxide (pH=12.4), which exists both in solution and crystal form in hardened Portland cement concrete. Large and extensive crystalline formations have been reported in young cement paste, where 25 percent of paste may be calcium hydroxide, as well as very old cement paste. It has been reported that calcium hydroxide provides both the bond as well as the load transfer mechanism between the aggregate and the cement mortar (calcium silicate hydrate).

C. SCOPE

The Air Force Civil Engineering Support Agency (AFCESA) was asked to identify the source of the problem and propose a solution in Logistic Need Statement 91034. This report summarizes the field investigation and laboratory work, supports conclusions, and offers recommendations on APU damage in the presence of spilled fluids.

D. METHODOLOGY

Air Force Civil Engineering Support Agency personnel visited several installations to see the damage first hand, and collect concrete samples. Laboratory work concentrated on (1) reproducing the field damage under controlled conditions, and (2) performing chemical analysis on field samples to assess the material alteration and its significance. The latter was undertaken because the damaged field specimens were friable and had a rancid smell.

E. TEST DESCRIPTION

1. Slab Tests. Work was initiated to reproduce the field damage under a controlled laboratory setting. This entailed heating the surface of two concrete slabs. One of the slabs was periodically treated with hydraulic and lubricating fluids and the other was kept dry.

2. Chemical Studies. Since the damaged specimens were friable, crumbly and rancid, they were thought to have been altered chemically. Consequently, a chemical study of the concrete was initiated at both the AFCESA Laboratory and the Materials Directorate of Wright Laboratory. This entailed Gas Chromatography/Mass Spectrometry (GC/MS) and Scanning Electron Microscopy (SEM) with X-ray Energy Dispersive Analysis (EDAX) at the AFCESA Laboratory; and GC/MS, Infrared Spectral Analysis (IR), and X-ray Diffraction (XRD) at the Wright Laboratory.

F. RESULTS:

1. Slab Tests. After four weeks of cyclically heating both slabs, damage was observed in the slab treated with hydraulic fluid and lubricating oil (turbo shaft oil). This was in the form of the same surface scaling noted in the field. There was no visual damage to the dry slab, which was not exposed to oils and fluids. Both slabs had been subjected to radiation heating (6-inch circular area, 350°F) of the surface for three hours each day, excluding weekends.

2. Chemical Tests. The SEM confirmed the presence of calcium hydroxide before the application of oils and heat, the GC/MS and IR showed that ester hydrolysis was occurring, and the XRD showed that calcium hydroxide was consumed. The presence or absence of calcium hydroxide in the damaged or undamaged areas has been validated by phenolphthalein solution.

G. CONCLUSIONS

Heat from the APU plays a significant role in the damage process, but not simply from a thermal fatigue aspect. Rather, the downward-directed heat facilitates and accelerates the chemical reaction that ultimately leads to scaling of the concrete.

With the application of APU heat, the free moisture in the top 1/4 to 1/2 inch of the concrete slabs is driven out. After the heat is turned off, and the pavement begins to cool, oils and fluids on the surface as well as free moisture from below are sucked into the pavement. Upon reheating, the calcium hydroxide in solution hydrolyzes with the esters found in the hydraulic fluid and lubricating oils, liberating the alcohol and forming calcium salts from the carboxylic (fatty) acids. The reaction rate doubles for every 10 degrees Celsius increase. For extensive heat durations (tens of minutes), and surface temperatures exceeding 212°F (100°C), the liquid moisture is converted to steam, expelling the oils, and the salts of the fatty acids are precipitated out in solid form. Upon cooling, the process repeats itself, and new oils are sucked in from the top and water from below.

Calcium hydroxide is being consumed in each cycle, since it provides the anion (OH-) for the hydrolysis reaction subsequently used in the formation of the alcohol; the calcium cation is used in the formation of the fatty acid salts. The salts, which are soft, slightly soluble, and white, replace the calcium hydroxide crystals. The reason why damage takes many months to become evident is because of the low solubility of calcium hydroxide in water.

H. RECOMMENDATIONS

The simplest solution to this problem is to keep all the hydraulic and lubricating oils off the pavement, especially the area of heat impingement. APU heat alone, will do little damage to the concrete. If oils cannot be kept off the pavement, the heat should not be allowed to impinge onto the spill areas. Heat enables oil penetration and the acceleration of the hydrolysis process. The use of steel plates at Dyess AFB (B-1) and Cecil Field (F/A-18) appears to be working because the pavement is shielded from heat.

If neither the heat nor oil can be kept off the pavement, sealants may prevent the oil from penetrating if the oils are not already in the concrete. It is believed that this approach may have little merit because the expelling steam may create pathways or they may develop from other causes (cracking). Also, the chemical composition of cement paste could be changed through the addition of pozzolans to diminish the calcium hydroxide content. However, this approach must be thoroughly tested since the esters may be attacking the sulphoaluminates as well. Finally, the Portland cement binder may have to be replaced by a neutral material (pH of 7) such as polymer concrete or ceramic. Several candidate materials are currently being tested in the laboratory to select potential solutions to the APU-oils problem.

I. TECHNOLOGY TRANSFER

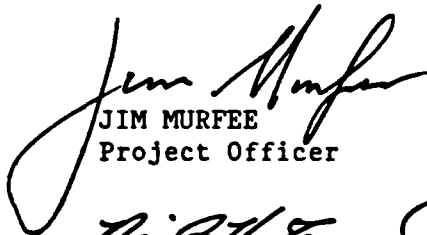
This research is transferable as knowledge of the problem only; solutions have yet to be identified.

PREFACE


This report was prepared by the Air Force Civil Engineering Laboratory, Tyndall Air Force Base, Florida 32403, under JON 2673-1021. Mr Jim Murfee was the Project Officer. This report summarizes work accomplished between June 1991 and September 1991. The authors appreciate the assistance of Dr Lee Smithson, Director of the Materials Integrity Branch located at Wright Materials Laboratory, Wright-Patterson AFB, Ohio.

This report has been reviewed by the Public Affairs Office and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.


This technical report has been reviewed and is approved for publication.




JIM MURFEE
Project Officer



NEIL F. FRAVEL, Lt Col, USAF
Chief, Engineering Research
Division



EDGAR F. ALEXANDER, GM-14
Chief, Air Base Operability
and Repair Branch



FRANK P. GALLAGHER III, Col, USAF
Director, Air Force Civil
Engineering Laboratory

TABLE OF CONTENTS

Section	Title	Page
I	INTRODUCTION.....	1
	A. OBJECTIVE.....	1
	B. BACKGROUND.....	2
	C. SCOPE OF WORK.....	2
II	WORK ACCOMPLISHED.....	4
	A. FIELD INVESTIGATION.....	4
	B. LABORATORY EFFORTS.....	7
	1. Slab Testing.....	7
	2. Chemical Studies.....	8
III	CONCLUSION AND RECOMMENDATIONS.....	13
	A. PROPOSED FAILURE MECHANISM.....	13
	B. RECOMMENDATIONS.....	16
	REFERENCES.....	18

LIST OF FIGURES

Figure	Title	Page
1	Pitted Concrete Surface Under APU.....	5
2	Damaged Piece of Concrete, Scale.....	5
3	Damage From Moving the Parking Space.....	6
4	Steel Plate Bolted to Concrete Under APU.....	6
5	Closeup of Paste-Aggregate Interface.....	7
6	Comparison of Injected Extract vs Octanoic Acid.....	11
7	Scanning Electron Micrograph of Calcium Hydroxide Crystals.....	12
8	Temperature and Liquid Saturation in a Concrete Slab Under a Heat Flux.....	13
9	Model of the Paste-Aggregate Interface.....	15

SECTION I

INTRODUCTION

A. OBJECTIVE

The objective of this research was to determine the causes of damage to concrete parking aprons under aircraft where auxiliary power units (APUs) impinge onto the concrete.

B. BACKGROUND

Both the United States Air Force and Navy have reported concrete damage on their respective B-1 and F/A-18 parking aprons. This damage is usually in the form of surface scaling. Base civil engineers report the damage to be in areas of APU jet blast impingement, where large amounts of spilled lubricants, hydraulic fluids and jet fuels have been noted. The fluids are either vented by the aircraft or spilled during maintenance.

APUs are found on many cargo aircraft such as C-5s and C-130s, bombers such as B-1s, and recently on fighter aircraft such as A-10s and F/A-18s. APUs were developed to start the main engines of the aircraft and to provide power for aircraft electrical and hydraulic systems without using the main engines. APUs are small turbojet engines with jet pipe exhaust temperatures of approximately 1100 to 1200°F (590 to 650°C), and exit velocities of about 300 mph. Most aircraft, with the exception of the B-1 and F/A-18, have their APU exhausts directed upward or out the side of the aircraft. However, the B-1s and F/A-18s exhaust from the bottom of the aircraft, approximately 60 and 40 inches above the pavement respectively, with angles of incidence of 45 degrees to the ground plane.

Navy reports (1) show maximum single exposure of concrete to an APU to be approximately 45 minutes; though, rarely more than 4 or 5 minutes. The B-1 APU usually runs 20 minutes or more, but may operate for hours. Both have reported surface temperatures from 330 to 400°F (165 to 205°C)

Each F/A-18 and B-1 aircraft has assigned apron parking spaces with severe limitations on deviation. Aircraft maintenance is performed on the aircraft while it is sitting on the parking apron. In the past, due to concrete scaling, the Navy often relocated their aircraft parking layouts to prevent foreign object damage (FOD). Also, the Navy and Air Force have tried the use of heat-resistant diabase aggregate, refractory concrete, and surface coatings (2). All resulted in a service life of one year or less. Steel plates, 1/4 inch thick, bolted to the pavement in the path of the APU exhaust impingement are in use at Dyess AFB (B-1) and Cecil Field (F/A-18). After four years of service at Cecil, the plates have prevented further concrete scaling; however, they pose a number of operational safety problems and are considered to be a temporary solution.

C. SCOPE OF WORK

The Air Force Civil Engineering Support Agency's (AFCESA) Operability and Repair Branch at Tyndall AFB, Florida was asked to identify the source of the problem and propose a solution (Logistic Needs Statement 91034). To this end, AFCESA personnel visited several installations to see the damage firsthand, and collect concrete samples. Laboratory work concentrated on (1) reproducing the field damage under controlled conditions, and (2) performing chemical analysis on field samples to

assess the material alteration and its significance. The latter was undertaken because the damaged field specimens were friable and had a rancid smell.

This report summarizes the field investigation and laboratory work, supports conclusions, and offers recommendations on APU damage in the presence of spilled fluids.

SECTION II
WORK ACCOMPLISHED

A. FIELD INVESTIGATION

Air Force Civil Engineering Support Agency personnel visited Cecil Field, FL (F/A-18), Beaufort MCAS, SC (F/A-18) and McConnell AFB, KS (B-1) in June and July of 1991 to survey reported damage and collect samples. Inspection revealed that all damage was confined to the APU impingement areas where large quantities of hydraulic fluid, lubricating oils and jet fuel were being spilled beneath the aircraft.

Figure 1 shows the damaged concrete surface (pitted), as well as the spilled fluids (dark area). The white areas are recently exposed mortar, where aggregate that was once within the concrete has popped out. Depths of oil penetration ranged from 1/2 to 3/4 of an inch for the initial damage and then progressed deeper with time. Figure 2 is a closeup of a freshly scaled piece of concrete. The size of the scale and the entrapment of large aggregate in the scale suggest that the problem is not caused by improper finishing. Figure 3 shows a larger damaged area which resulted from relocating the aircraft parking spaces. Figure 4 displays the steel plate currently employed at Dyess AFB (B-1) and Cecil Field (F/A-18). The damage in front of the plate occurred before the parking space was relocated to direct the blast onto the steel plate. Recently, the plates at Cecil were taken up, after 4 years of service, to replace the concrete joint seals and no damage was observed to the concrete underneath.



Figure 1 Pitted Concrete Surface Under APU

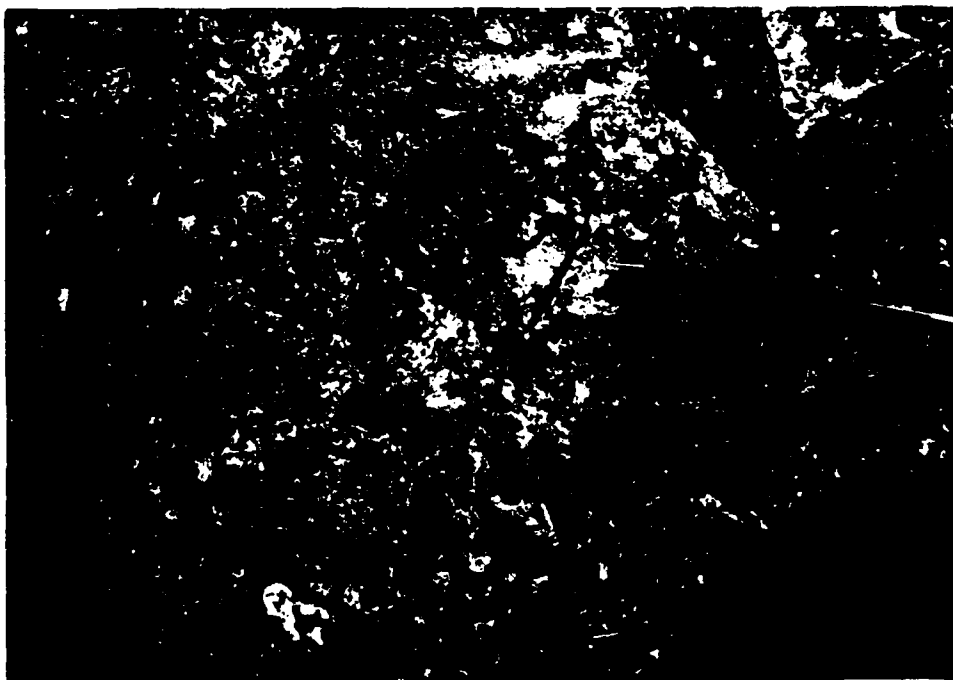


Figure 2 Damaged Piece of Concrete, Scale



Figure 3 Damage from Moving the Parking Space

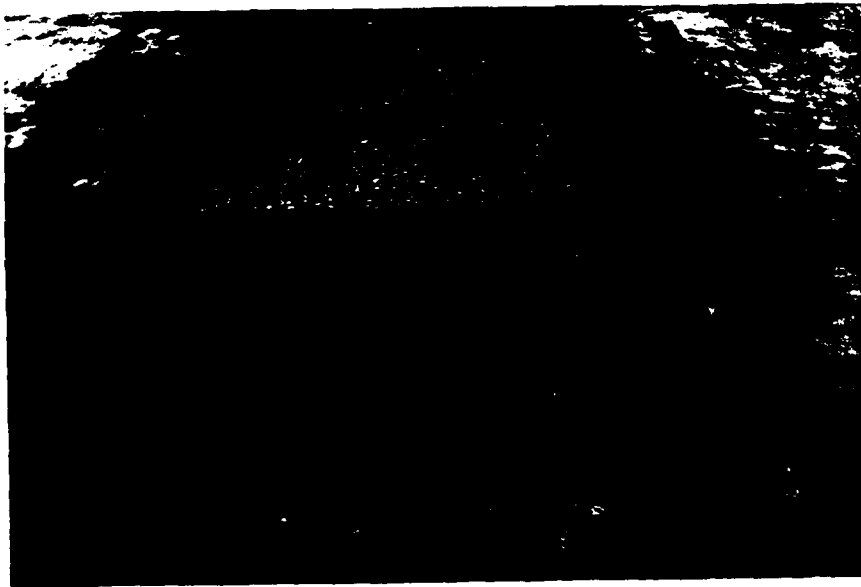


Figure 4 Steel Plate Bolted to Concrete Under APU

Observation of full-depth 4- and 6-inch diameter cores taken from the damaged areas revealed lubricant penetration from 1/2 to 3/4 inch. All of the damaged concrete (Figures 1 to 4) showed large amounts of exposed aggregate. The concrete appeared to be delaminating at the paste-aggregate interface (Figure 5). Further damage involves the removal of individual large aggregate, one at a time. Cores taken outside the zone of APU impingement, but within the fluid spill area, showed minor surface damage and minimal fluid penetration.



Figure 5 Closeup of Paste-Aggregate Interface

B. LABORATORY EFFORTS

1. Slab Testing. Work was initiated to reproduce the field damage under a controlled laboratory setting. This entailed heating the surface of two concrete slabs, 3 feet in diameter by 4 inches thick, under cyclic conditions. One of the slabs was periodically treated with hydraulic and

lubricating fluids and the other was kept dry.

After four weeks of cyclically heating both slabs, damage was observed in the slab treated with hydraulic fluid and lubricating oil (turbo shaft oil). This was in the form of the same surface scaling noted in the field. There was no visual damage to the dry slab, which was not exposed to oils and fluids. Both slabs had been subjected to radiation heating (6-inch circular area, 350°F) of the surface for three hours each day, excluding weekends. No tests were performed with jet fuels, and testing of lubricating oil or hydraulic fluid separately was not performed.

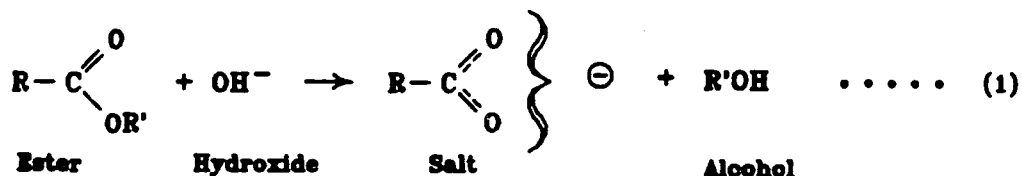
2. Chemical Studies. Since the damaged specimens were friable, crumbly and rancid, they were thought to have been altered chemically. Consequently, a chemical study of the concrete was initiated at both AFCESA and the Materials Directorate of Wright Laboratory. This entailed Gas Chromatography/Mass Spectrometry (GC/MS) and Scanning Electron Microscopy (SEM) with X-ray Energy Dispersive Analysis (EDAX) at AFCESA; and GC/MS, Infrared Spectral Analysis (IR), and X-ray Diffraction (XRD) at Wright Laboratory. This work was undertaken because it was thought that the esters in lubricating oils (MIL-L-7808 for Air Force, and MIL-L-23699 Navy) and hydraulic fluids (MIL-H-83282) could have been hydrolyzing. Of the two major constituents of the spilled fluids, hydrocarbons and esters, only the latter has been known to be detrimental to concrete (3).

Esters, which are chemically-combined acids and alcohols, will break down (hydrolyze) when heated in an aqueous acid or base solution (4). Discussions with Hatco, a major manufacturer of raw materials in lube

oils and hydraulic fluids, reveal that 90-95 percent of lubricating oils are composed of ester blends. Hydraulic fluid (MIL-H-83282) is 60-70 percent hydrocarbons and 30-35 percent esters.

If the oils and/or hydraulic fluids were undergoing hydrolysis, it would have to be of an alkaline variety, since the pH of concrete may be as high as 11 or 12. This is due to the strong base (5) calcium hydroxide $[Ca(OH)_2, pH=12.4]$, which exists both in solution and crystal form in hardened Portland cement concrete. Large and extensive crystalline formations have been reported in young cement paste (6), where 25 percent of paste may be calcium hydroxide, as well as very old cement paste (7). It has been reported that calcium hydroxide provides both the bond as well as the load transfer mechanism between the aggregate and the cement mortar (calcium silicate hydrate) (8).

The reaction (4):



under alkaline conditions, produces the salt of the carboxylic acid and liberates the alcohol. In this reaction, the calcium hydroxide provides the OH^- anion and the calcium cation is used in the formation of the acid salt. Calcium salts of the fatty acids are slightly soluble in water, a polar medium, and insoluble in hexane, a nonpolar solvent, whereas the acids are the reverse.

In order to determine the origin of the scaled products, samples of the damaged concrete were crushed and mixed with an aqueous solution of sodium chloride and filtered, at two independent sites, AFCESA and Wright Material Labs. The filtered wash was then split into two portions with one portion being mixed with hexane, which was subsequently extracted and injected into a HP gas chromatography device. This ensured that the aqueous sodium chloride wash did not contain any hydraulic fluids or lubricating oils. The second portion of the sodium chloride wash was mixed with concentrated hydrochloric acid which would convert any salts present into their fatty (carboxylic) acid counterparts. Hexane was added; the whole mixture was shaken; then the hexane was extracted and injected into the gas chromatography/mass spectrometer device. At AFCESA, this procedure revealed the presence of hexanoic, octanoic, and nonanoic acids. Wright Materials Lab used water alone for their extraction, and found hexanoic, octanoic and decanoic acids. All of these are straight-chain fatty acids found in the esters of turboshaft oil (MIL-L-7808 or MIL-L-23699). Figure 6 compares one of the mass spectra taken at AFCESA of the injected extract vs the library value. The computer was over 80 percent confident it was octanoic acid. Infrared spectroscopic analysis performed at Wright Materials Lab on the aqueous wash revealed the structural carbonyl (C=O) and hydroxyl (OH) groups contained in carboxylic acids. These acids were all derived from the precipitated calcium salts found in the scaled material.

X-Ray Diffraction (XRD) analysis of the scaled concrete specimens at Wright Lab revealed the presence of quartz and calcium carbonate (limestone), but no calcium hydroxide [Ca(OH)₂].

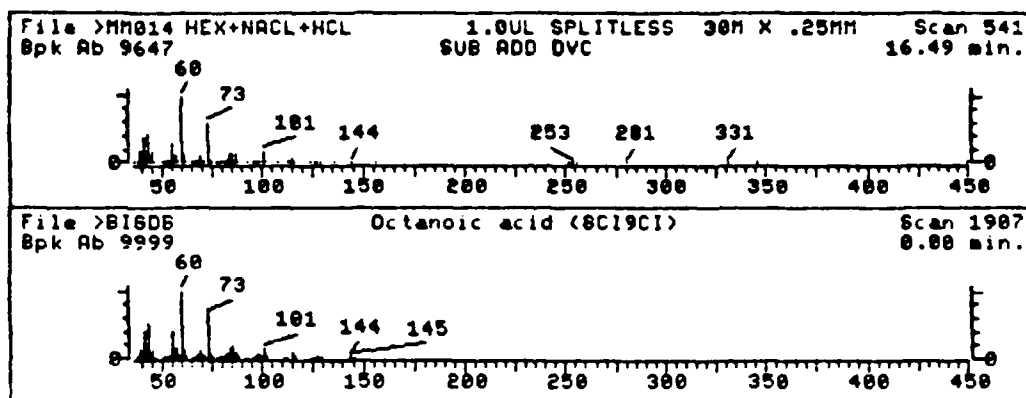


Figure 6 Comparison of Injected Extract vs Octanoic Acid

The calcium hydroxide has been converted to limestone by the carbon dioxide in the air or in the jet exhaust. To confirm the conversion, the top 0.25 inch was sliced off a core taken from inside the damaged area and treated with a solution of phenolphthalein and alcohol. If the solution contacts a base with a pH greater than 9 to 10, such as calcium hydroxide, it will turn violet. The original exposed surface of the slice of core, which had been converted to limestone, did not change color; however, the paste areas on the bottom turned almost completely violet. Treating the bottom of the scaled pieces with phenolphthalein showed small violet areas but nothing substantial, and none of the exposed aggregate surfaces were violet. A scanning electron microscopic investigation of the bottom of the thin section revealed the classical hexagonal platelets (9) as shown in Figure 7.

In summary, the SEM confirms the presence of calcium hydroxide before the application of oils and heat, the GC/MS and IR show that ester hydrolysis is occurring, and the XRD showed that calcium hydroxide was consumed. The presence or absence of calcium hydroxide in the damaged or undamaged areas has been validated by phenolphthalein solution.

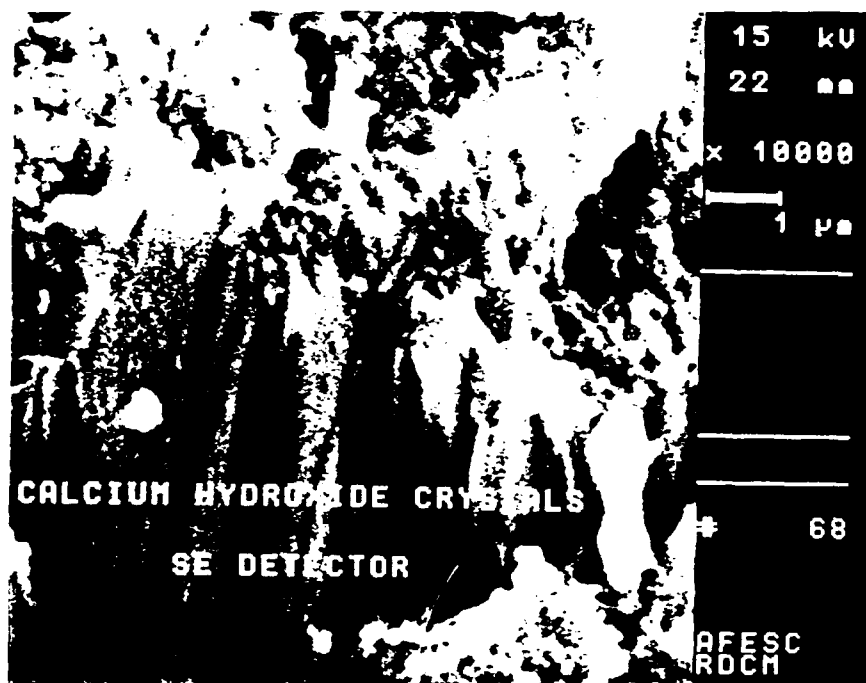


Figure 7 Scanning Electron Micrograph of Calcium Hydroxide

A literature review (10) and discussion with Dr Bob Tapscott of New Mexico Engineering and Research Institute (NMERI), revealed that both JP-4 and JP-5 jet fuels contain carboxylic acids as corrosion inhibitors. These acids, which vary in concentration from 10 to 55 mg/l, depending on the manufacturer, will also dissolve the calcium hydroxide $[\text{Ca}(\text{OH})_2]$, as well as possibly calcium monosulfoaluminate hydrate (3). This could explain the loss in strength of samples soaked in jet fuel reported by others (10).

III CONCLUSIONS AND RECOMMENDATIONS

A. PROPOSED FAILURE MECHANISM

Heat from the APU plays a significant role in the damage process, but not simply from a thermal fatigue aspect. Rather, the downward-directed heat facilitates and accelerates the chemical reaction that ultimately leads to scaling of the concrete.

With the application of APU heat, the free moisture in the top 1/4 to 1/2 inch of the concrete slabs is driven out (upward and downward). This is supported by Figure 8 which shows the liquid saturation in rock exposed to a radiation heat source. After the heat is

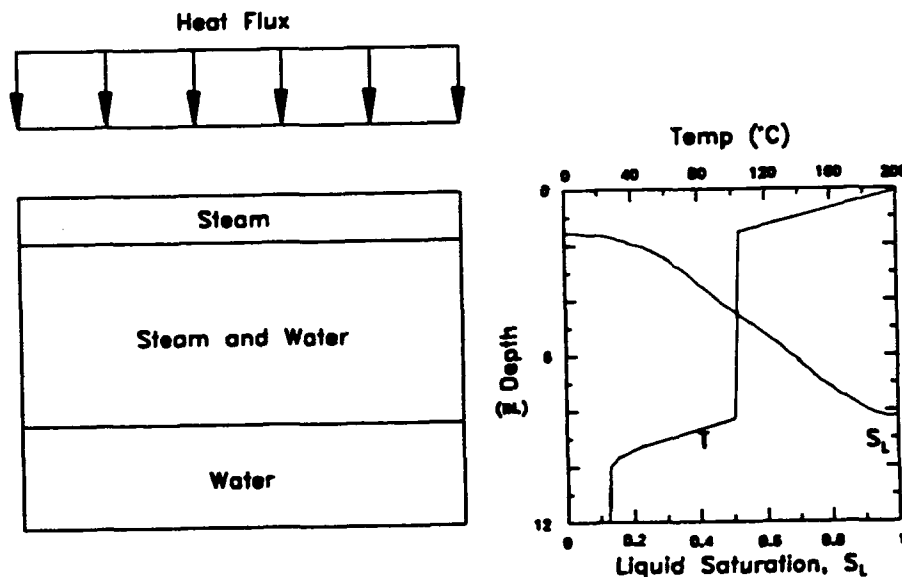


Figure 8 Temperature and Liquid Saturation in a Concrete Slab under a Heat Flux (11)

turned off, and the pavement begins to cool, oils and fluids on the surface as well as free moisture from below are then sucked into the pavement. For instance, rock or concrete with a liquid saturation of 0.2

percent or less has suction pressures (13) on the order of 100 bars (1450 psi). Upon reheating, the calcium hydroxide in solution hydrolyzes with the esters found in the hydraulic fluid and lubricating oils, liberating the alcohol and forming calcium salts from the carboxylic (fatty) acids. A rule of thumb for hydrolysis is that the reaction rate doubles for every 10 degrees Celsius increase (4). For extensive heat durations (tens of minutes), and surface temperatures exceeding 212°F (100°C), the liquid moisture is converted to steam, expelling the oils, and the salts of the fatty acids are precipitated out in solid form. Upon cooling, the process repeats itself, that is new oils are sucked in from top and water from below.

Calcium hydroxide is being consumed in each cycle. That is, it provides the anion (OH-) for the hydrolysis reaction subsequently used in the formation of the alcohol; the calcium cation is used in the formation of the fatty acid salts. The salts, which are soft, slightly soluble, and white (or tinged red from hydraulic fluid dyes), replace the calcium hydroxide crystals. The reason why damage takes many months to become evident is because of the low solubility of calcium hydroxide in water.

Figure 9 illustrates the contact between the cement mortar (calcium silicate hydrate) and the aggregate in an early stage of the hydration process (8). With time and increased hydration, the intermediate layer is overlapped by more of the panel-shaped calcium hydroxide crystals and the cement mortar. Zimbelmann (8) states that the load transfer between the cement mortar and the aggregate is provided mainly by the large hexagonal platelets of calcium hydroxide $[\text{Ca}(\text{OH})_2]$.

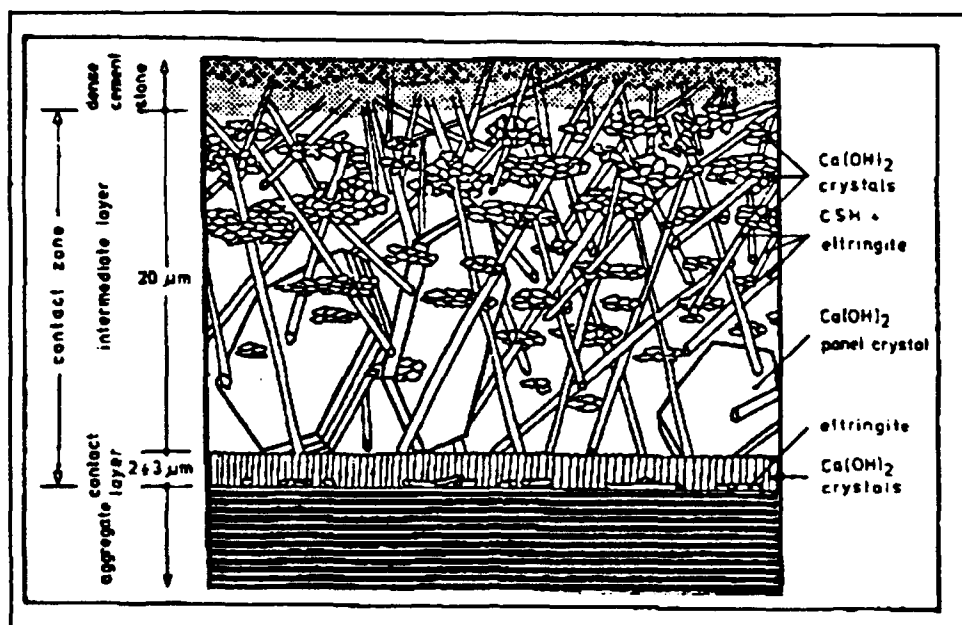


Figure 9 Model of Paste-Aggregate Interface

Both the contact layer around the aggregate and the large platelets of calcium hydroxide are being consumed in the hydrolysis process.

Although 70 percent of concrete volume is aggregate, finishing brings the cement paste mortar to the surface, leaving most of the large aggregate 1/4 to 1/2 inch below the surface. Assuming that (1) aggregate volume (70%) is equated to cross-sectional area and (2) failure is stress dependent, the concrete strength could be reduced by as much as 70 percent due to loss of bond between the paste and aggregate. Upon further heating cycles, the thermal differential stresses will exceed the strength of the cement mortar separating the aggregate, resulting in a planar failure or scaling of 1/4 to 1/2 inch in thickness.

B. RECOMMENDATIONS

The damage to concrete from oils is not new. Lea (3) states ". . . esters are broken up by hydrolysis into their constituent alcohol and acid components. This process, termed saponification, can be produced by the action of acid or alkali solutions ... the extent to which an oil can attack a concrete is dependent on the ease with which it can penetrate the material." As a matter of record, in the 1930s and 1940s, the amount of calcium hydroxide in set cement was determined by ester hydrolysis (acetoacetic ester) developed by Franke (7).

In the case of the APU impingement on concrete parking areas under B-1 and F/A-18 aircraft, the combination of heat and lubricating or hydraulic oils results in surface scaling. The heat makes it possible for the oils to penetrate the concrete, accelerating the hydrolysis process. Hydrolysis turns all the calcium hydroxide around the aggregates into salts of fatty acids and destroys the paste-aggregate bonds.

The simplest solution to this problem is to keep all the hydraulic and lubricating oils off the pavement, especially the area of heat impingement. APU heat alone, will do little damage to the concrete. If oils cannot be kept off the pavement, the heat should not be allowed to impinge onto the spill areas. Heat enables oil penetration and the acceleration of the hydrolysis process. The use of steel plates at Dyess AFB (B-1) and Cecil Field (F/A-18) appears to be working because the pavement is shielded from heat.

If neither the heat nor oil can be kept off the pavement, sealants may prevent the oil from penetrating. This has been tried by the Navy (2), but at the time of application, the oils were already in the concrete.

It is believed that this approach may have little merit because the expelling steam may create pathways or they may develop from other causes (cracking). Also, the chemical composition of cement paste could be changed through the addition of pozzolans to diminish the calcium hydroxide content. However, this approach must be thoroughly tested since the esters may be attacking the sulphoaluminates (8) as well. Finally, the Portland cement binder may have to be replaced by a neutral material (pH of 7) such as polymer concrete or ceramic. Several candidate materials are currently being tested in the laboratory, to select potential solutions to the APU-oils problem.

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